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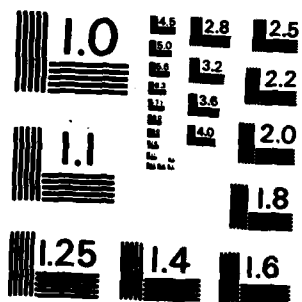               OF CHEMISTRY  B J FISHER ET AL. 04 NOV 83
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Mono- and Binuclear Iridium Carbonyl Hydrides

Containing Di(tertiaryphosphine) Ligands

By

Barbara J. Fisher and Richard Eisenberg

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New mono- and binuclear iridium(I) carbonyl halide complexes containing the di(tertiaryphosphine) ligands $Ph_2P(CH_2)_nPPh_2$ (n=2, dppe; n=3, dppp) have been prepared, and the formation of iridium(III) hydrides by $H_2$ oxidative addition has been studied. The binuclear complexes $[IrX(CO)(dppp)]_2$ (X = Br, I) possess trans phosphine donors with the dppp ligands bridging the Ir(I) centers. Addition of $H_2$ yields the tetrahydride species $[IrH_2X(CO)(dppp)]_2$ in which the trans phosphine arrangement at each iridium is maintained. However, upon heating, cleavage of the dimers is noted,

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leading to the mononuclear species $IrH_2X(CO)(dppe)$. For X = I, mononuclear dppe complexes are also prepared starting with the reaction of $IrI_2(CO)_2^-$ + dppe under CO to yield $IrI(CO)_2(dppe)$. All of the dppe complexes are mononuclear with dppe acting as a chelate. The necessarily cis disposition of phosphine donors in the mononuclear chelates is readily evidenced by $^1H$ nmr spectroscopy of the hydride complexes. Reversible addition of CO to $IrX(CO)(dppe)$ (X = Br, I) is also observed.

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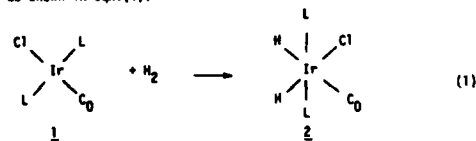Availability Codes

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Mono- and Binuclear Iridium Carbonyl Hydrides Containing Di(tertiaryphosphine)
Ligands

Barbara J. Fisher and Richard Eisenberg*

## Abstract

New mono- and binuclear iridium(I) carbonyl halide complexes containing
the di(tertiaryphosphine) ligands $Ph_2P(CH_2)_nPPh_2$ (n=2, dppe; n=3, dppp) have
been prepared, and the formation of iridium(III) hydrides by $H_2$ oxidative
addition has been studied. The binuclear complexes $[IrX(CO)(dppp)]_2$
(X = Br, I) possess trans phosphine donors with the dppp ligands bridging
the Ir(I) centers. Addition of $H_2$ yields the tetrahydride species
$[IrH_2X(CO)(dppp)]_2$ in which the trans phosphine arrangement at each iridium
is maintained. However, upon heating, cleavage of the dimers is noted,
leading to the mononuclear species $IrH_2X(CO)(dppp)$. For X = I, mononuclear
dppp complexes are also prepared starting with the reaction of $IrI_2(CO)_2^-$
+ dppp under CO to yield $IrI(CO)_2(dppp)$. All of the dppe complexes are
mononuclear with dppe acting as a chelate. The necessarily cis disposition
of phosphine donors in the mononuclear chelates is readily evidenced by
$^1H$ nmr spectroscopy of the hydride complexes. Reversible addition of CO
to $IrX(CO)(dppe)$ (X = Br, I) is also observed.

**Introduction** Metal hydrides play an important role in many metal catalyzed
reactions such as hydrogenation, hydroformylation, the water gas shift reaction,
and CO reduction chemistry.[1] For this reason, the preparation and reaction
chemistry of transition metal hydride complexes have been studied extensively.
The oxidative addition of $H_2$ to a metal complex is one of the most important
methods of hydride preparation, and one of the most relevant in the context of
catalytic properties, since this reaction represents a principal mode for the
activation of $H_2$. Since Vaska's initial report in 1962,[2] it has been known
that $d^8$ iridium(I) phosphine complexes are particularly active with regard to
$H_2$ oxidative addition.[1c] This reaction invariably proceeds with cis stereo-
chemistry at the metal center, and in the case of trans-$IrCl(CO)(PPh_3)_2$ and its
analogs, results in products in which the phosphine ligands maintain their trans
disposition as shown in eqn.(1).

$$\underset{\underline{1}}{\overset{\begin{array}{c} \;Cl \qquad\; L \\ \diagdown \; | \diagup \\ Ir \\ \diagup \; | \diagdown \\ L \qquad\; C_O \end{array}}{}} \;+\; H_2 \;\longrightarrow\; \underset{\underline{2}}{\overset{\begin{array}{c} H \quad | \quad Cl \\ \diagdown | \diagup \\ Ir \\ \diagup | \diagdown \\ H \quad L \quad C_O \\ L \end{array}}{}} \tag{1}$$

L = tertiary phosphine

In this paper, we describe our studies on the synthesis, characterization
and $H_2$ oxidative addition chemistry of new iridium complexes containing
di(tertiary phosphine) ligands. These ligand systems may either chelate a
single metal center or bridge two Ir ions. The former leads to a cis stereo-
chemistry of phosphine donors different from that observed in most adducts of
Vaska's complex and its analogs, while the latter produces two metal centers
in close proximity for the binding and activation of substrates.

The relative tendency of the di(tertiary phosphine) ligand system

$Ph_2P(CH_2)_nPPh_2$ to bridge or chelate is shown in eqn.(2) as reported by Sanger. In this reaction, only a monomer is synthesized when n=2, whereas dimers form when n=1 and 3.[3] Compound 3, which was first reported by Vaska, forms because of the favorable driving force of five-membered chelate ring formation.[4] Complexes 4 and 5, on the other hand, maintain what seems to be the electronically favorable disposition of trans P donors with the creation of face-to-face dimers of Ir(I) having ligand sets similar to that found in Vaska's complex.



$$[IrCl(cod)]_2 \ + \ Ph_2P(CH_2)_nPPh_2 \ + \ CO \ \longrightarrow \quad (2)$$

n = 1 dppm
n = 2 dppe
n = 3 dppp
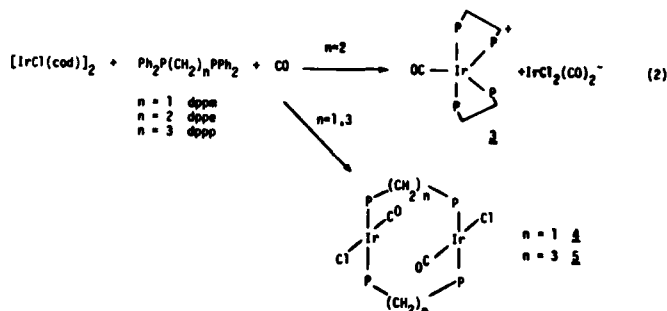
Our interest in dimeric compounds of this type was stimulated by the notion of two metal centers in close proximity for the activation of two substrates simultaneously, or for the activation of a single substrate using both metal centers and their attendant 4e's (two $d^8 \rightarrow d^6$ oxidative additions on a single substrate). Use of dppm as a bridging ligand has been explored extensively in face-to-face dimers and in A-frame complexes, and yields a relatively rigid binuclear structure in which metal···metal distances vary between 2.7 and 3.5 Å.[5] The dppp ligand, on the other hand, allows a more flexible binuclear structure with metal···metal distances ranging up to 6 Å.[6] The chemistry of these systems has only begun to be explored. Pignolet and Wang have found that 5 oxidatively

adds $H_2$ to form a mixture of the dihydride $[Ir_2H_2(CO)_2Cl_2(dppp)_2]$, 6, and the tetrahydride $[Ir_2H_4(CO)_2Cl_2(dppp)_2]$, 7 in eqn.(3).[6]



$$5 \ + \ H_2 \ \xrightarrow{CH_2Cl_2} \qquad + \qquad \qquad (3)$$
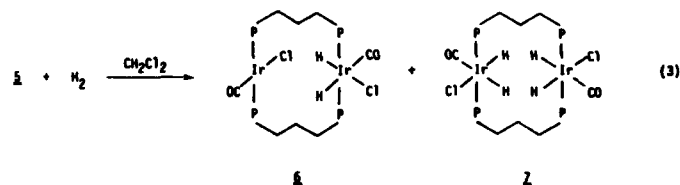
The structural assignments of 6 and 7 are supported by crystallographic evidence. Loss of $H_2$ from 7 appears facile, and the increased steric bulk at one Ir center after the first oxidative addition appears to inhibit reactivity at the second metal center.

The studies described in this paper use the work of Sanger and Pignolet as a starting point. Because the bromo and iodo analogs of Vaska's complex were known to be more reactive than the parent chloro system, $IrCl(CO)(PPh_3)_2$,[7] we commenced studies on the bromo and iodo analogs of 5. The context in which our studies were undertaken was the development of $H_2$ reduction catalysts for $CO_2$, a goal that still remains to be reached. Based on Herskovitz' work, it was known that electron rich Ir(I) centers are capable of reacting with $CO_2$ to form metallocarboxylate species.[8] We envisioned that the presence of nearby hydrides on a second metal center would facilitate the desired reduction of bound $CO_2$.

The investigations which we outline here include studies of binuclear dppp complexes and the hydrides which they form, the unexpected cleavage of these dimers into mononuclear species, as well as the formation and reaction chemistry of previously unknown mononuclear complexes containing only a single di(tertiary

phosphine) ligand. These mononuclear complexes represent cis-phosphine analogs
of the well studied $IrX(CO)L_2$ system.

## Experimental Section

**Physical Measurements.** Microanalyses were performed by Galbraith Laboratories.
Infrared spectra were recorded on a Perkin-Elmer 467 Grating Infrared Spectro-
photometer. $^1H$ nmr spectra were recorded with a Bruker WM-400 400 MHz spec-
trometer. $^{31}P$ nmr spectra were recorded with a JEOL FT 100 spectrometer at
41.25 MHz or a Bruker WM-400 spectrometer at 162 MHz. Gas chromatography was
done on a Hewlett Packard 5700A g.c. interfaced with a Hewlett Packard 3380A
Automatic Integrator.

Carbon monoxide was detected on either 12 feet of Poropak Q or 2 feet of
Molecular Sieves 5A. Molecular $H_2$ was detected on the molecular sieves column.
In all g.c. detection, 1/4" columns were used at 42°C using He as the carrier
gas and thermal conductivity detectors. The flow rate of He was 36-48 mL/min.,
and retention times of 1.05 and 1.35 minutes were observed for $H_2$ and CO,
respectively, on the Poropak Q column, and 0.31 and 4.1, respectively, on the
molecular sieves column.

**Reagents.** All operations were performed under $N_2$, CO or $H_2$ using modified
Schlenck techniques. Tetrahydrofuran and benzene were dried over Na and
distilled under $N_2$ before use. Bis(diphenylphosphino)ethane (dppe) and
bis(diphenylphosphino)propane (dppp) were purchased from Strem Chemical and
recrystallized from boiling ethanol. Bio beads were purchased from Bio-Rad.
Tetramethylene sulfone (sulfolane) was purchased from Aldrich and distilled
twice (first time from $P_2O_5$) immediately prior to use. All other reagent grade
chemicals were purchased commercially and used without further purification.
Throughout TBA = tetra-n-butylammonium.

[TBA][Ir(CO)$_2$Br$_2$]. Cleare and Griffith's procedure for preparing the analogous
Rh compound was followed.[9] Typically $IrCl_3 \cdot (H_2O)_3$ (1 g) and KBr (1 g) were
refluxed in a 1:1 (v/v, 20 mL) mixture of formic acid and HBr. The system

was open only to a mineral oil bubbler, allowing the $CO_2$ generated during the reduction to escape. After 12 to 24 hours, the solution had turned pale yellow. (If the solution had not turned pale yellow in 24 hours, an additional 1-2 mL of formic acid was added, and the refluxing continued until a pale yellow solution was obtained.) After cooling under a moderate stream of $N_2$, tetrabutylammonium bromide (1 g in 5 mL of $H_2O$) was added. The product precipitated as a yellow powder. An additional 10 to 20 mL of water were added and the solution cooled on an ice bath to insure an almost quantitative yield. The product was washed with cold water, ethanol and ether. The product was recrystallized from boiling isopropanol. The product was also obtained in good yield by Forster's method (see below).

[TBA][Ir(CO)$_2$I$_2$]. Forster's procedure was followed.[10] Typically $IrCl_3 \cdot (H_2O)_3$ (1 g) and NaI (1 g) were refluxed in 30 mL of 5% $H_2O$ in 2-methoxyethanol under an extremely slow flow of CO, ca. 5 mL/min. After about 12 hours, the solution had turned pale yellow. The solution was cooled under a stream of CO to room temperature, and tetrabutylammonium iodide (1 g in 30 mL of $H_2O$) was added. The product precipitated as a yellow powder. The product was washed with cold water, cold isopropanol and pentane, and was recrystallized from boiling isopropanol. The product is air sensitive, and should be prepared immediately before use, or stored under vacuum.

[Ir$_2$Cl$_2$(CO)$_2$(dppp)$_2$], 5. This complex was prepared by Sanger's method.[3] yield, ca. 80%.

[Ir$_2$Br$_2$(CO)$_2$(dppp)$_2$], 8. A solution of 0.54 g (0.83 mmoles of [TBA][IrBr$_2$(CO)$_2$] and 0.3 g (0.83 mmoles) of dppp was stirred in acetone (15 mL) for 24 hours. The yellow solution initially evolved CO. A pale precipitate formed after about 15 minutes; the solution cleared after an additional 15-30 minutes. The desired product began to precipitate after 1 h, but the solution was allowed to stir for an additional 8 h. The yellow precipitate was washed with cold acetone, and

$Et_2O$. The isolated powder was analytically pure. Yield: 0.49 g, 84%. Anal. Calcd. for Ir$_2$C$_{56}$H$_{52}$O$_2$P$_4$Br$_2$: C, 47.1; H, 3.7; P, 8.7. Found: C, 46.5; H, 3.8; P, 8.5. The remainder of the product can be isolated by the addition of $H_2O$ (0.5 mL) to the filtrate and stirring overnight.

[Ir$_2$I$_2$(CO)$_2$(dppp)$_2$], 9. Wang and Pignolet's method[6] was modified as follows. LiI (2 g) in EtOH (ca. 30 mL) was added to a slurry of 0.15 g [Ir$_2$Cl$_2$(CO)$_2$(dppp)$_2$] in benzene (ca. 20 mL). The solution was heated at 60°C and the yellow precipitate monitored by i.r. After 6 h, the metathesis of I$^-$ for Cl$^-$ was complete as shown by shift of $\nu_{CO}$ in the IR. ($\nu_{CO} = 1950$ cm$^{-1}$ for 9 and $\nu_{CO} = 1940$ for [Ir$_2$Cl$_2$(CO)$_2$(dppp)$_2$]). The precipitate was filtered, and washed with EtOH and $Et_2O$.

[Ir$_2$H$_4$Br$_2$(CO)$_2$(dppp)$_2$], 10. A 0.5 g (0.35 mmoles) sample of 8 was dissolved in 100 mL of $CH_2Cl_2$. The solution was pumped and flushed with $H_2$ several times and then stirred vigorously under ca. 1 atm of $H_2$. After 24 h, the solution had lost its yellow color. The product precipitated as a colorless powder after the addition of 20 mL of 99% EtOH, followed by removal of ca. 20 mL of $CH_2Cl_2$. Yield: 0.42 g, 84%. Anal. Calc. for Ir$_2$C$_{56}$H$_{56}$O$_2$P$_4$Br$_2$: C, 47.1; H, 3.9; P, 8.7; Br, 11.2. Found: C, 47.0; H, 4.0; P, 8.5; Br, 11.4.

[Ir$_2$H$_4$I$_2$(CO)$_2$(dppp)$_2$], 11. A 0.2 g (0.13 mmoles) sample of 9 was dissolved in 10 mL of THF, and placed under an atmosphere of $H_2$. The solution rapidly lost its yellow color (ca. 0.5 h), but was allowed to stir at room temperature for 8 h. Ethanol (20 mL) was added, and THF was removed until the product precipitated as a colorless powder. The product can be recrystallized from hot $CH_2Cl_2$ under $H_2$.

$[Ir_2H_2Br_2(CO)_2(dppp)_2]$, **12**. A 0.1 g (0.07 mmoles) sample of **8** was dissolved in 15 mL of $CH_2Cl_2$ and diluted with 15 mL THF. The solution was thoroughly degassed and placed under $N_2$. One equivalent (1.7 mL, 0.07 mmoles) of $H_2$ at 1 atm was added using a pressure-lok gas tight syringe. The solution was vigorously stirred for 24 hours. Ethanol (15 mL) was added and the $CH_2Cl_2$/THF mixture removed until the product precipitated as a yellow powder. Yield: 0.8 g, 80%.

$IrI(CO)_2(dppp)$, **13**. A 0.14 g sample of dppp in 10 mL of THF was added to 0.26 g of $[TBA][IrI_2(CO)_2]$ under CO. The solution was stirred at room temperature under CO overnight, during which time crystalline [TBA]I precipitated. Ethanol (ca. 5 mL) was added, resulting in the dissolution of the [TBA]I and the precipitation of a colorless material. (This colorless precipitate has one $\nu_{CO} = 1930$ cm$^{-1}$, and was identified as $Ir(dppp)_2(CO)I$ by analogy to the known $Ir(dppe)_2(CO)Cl$ which is colorless and has one $\nu_{CO} = 1933$ cm$^{-1}$.)[3,4] The yellow solution was filtered away from the precipitate and the THF removed by rotary evaporation until the desired product precipitated as a bright yellow powder. Yield: 0.15 g, 57% Anal. Calc. for $IrC_{29}H_{26}O_2P_2I$: C, 44.2; H, 3.3; P, 7.9. Found: C, 44.27; H, 3.54; P, 8.09.

$IrH_2I(CO)(dppp)$, **14**. A sample of **13** was dissolved in EtOH/THF (ca. 1:4, v/v) under $H_2$, and $H_2$ was slowly bubbled through the solution (ca. 5 mL/min). After 12 h the solution was colorless, and the product had started to precipitate. Vigorous bubbling of $H_2$ through the solution resulted in the precipitation of the rest of the product as a colorless powder. The product was filtered in air, washed with pentane, and recrystallized from hot $CH_2Cl_2$ under $H_2$. Yield: >90%.

$IrH_2Br(CO)(dppp)$, **15**. A 0.1 g (0.07 mmoles) sample of **10** was dissolved in 10 mL of $CH_2Cl_2$ and diluted with 20 mL of THF. Triethylamine (1 mL) was added, and the solution placed under ca. 1 atm of $H_2$. The solution was stirred at 65° for 12-24 hours. The solvent (including triethylamine) was removed under vacuum. The solids were dissolved in a minimum volume of acetone, and water was added until the product began to precipitate, usually as a cream colored powder. The product can be recrystallized from hot $CH_2Cl_2$ under $N_2$. Complex **14** can be prepared by this method from complex **11**, but at least 24 hours of heating is required.

$IrBr(CO)(dppe)$, **16**. A 0.1 g (0.25 mmoles) sample of dppe dissolved in ca. 7 mL of THF was added to 0.16 g (0.25 mmoles) of $[TBA][IrBr_2(CO)_2]$ dissolved in 5 mL of THF cooled to -70°C. The solution was allowed to warm to room temperature over 30 min. Ethanol (10 mL) was added to the reaction solution which was then reduced in volume using a rotary evaporator until the product crystallized as bright orange microcrystals. Yield: 0.13 g, 75%.

$IrI(CO)(dppe)$, **17**. A 0.1 g (0.25 mmoles) sample of dppe dissolved in ca. 7 mL of THF was added to 0.2 g (0.26 mM) of $[TBA][IrI_2(CO)_2]$ dissolved in ca. 5 mL THF. The mixture was heated to 60°C for 15-20 min before cooling to room temperature. After this time, the yellow solution turned bright orange. Ethanol (10 mL) was then added to the orange solution and solvent removed until the product precipitated as an orange powder. The product is recrystallized from hot benzene/EtOH. Yield: 0.1 g, 90%. Anal. Calcd. for $IrC_{27}H_{24}OP_2I$: C, 43.5; H, 3.2; P, 8.3. Found: C, 43.7; H, 3.5; P, 8.38.

$IrH_2X(CO)(dppe)$ (X = Br(**18**), I(**19**)). A sample of **16** or **17** was dissolved in benzene under a $H_2$ atmosphere and stirred until the solution lost its orange

color ($\leq$ 3 min). After the addition of EtOH, bubbling of $H_2$ through the reaction solution was continued for several hours until the product precipitated as a colorless powder. Yield, >90%. This procedure results in isolation of the thermodynamic isomer of 18 or 19 which is described in the Results section.

IrX(CO)$_2$(dppe) X = Br, 20, X = I, 21. An orange benzene solution of 16 or 17 is placed under CO. The solution turns yellow immediately, with a corresponding change in the solution spectra. The CO adducts are difficult to isolate as solids because of CO loss. Solution yield, 100%, based on $^1$H and $^{31}$P nmr spectra.

Molecular Weight Determination by Bio Bead Filtration. Bio Beads SX-4 (ca. 30 mL) were placed in boiling $CH_2Cl_2$ and allowed to percolate in the refluxing solvent for 15 min, after which the mixture was allowed to cool. A 50 mL buret was packed with the beads using $CH_2Cl_2$ as the eluent. A calibration curve for molecular weight was made using seven rhodium and iridium phosphine complexes in the following procedure. As much compound as possible was dissolved in 0.5 mL of $CH_2Cl_2$, and loaded onto the column, and eluted with $CH_2Cl_2$ (dispensed from an addition funnel). The time for elution of each complex was measured and plotted against log (molecular weight) to give a straight line. The new complex, [Ir$_2$Br$_2$(CO)$_2$(dppp)$_2$], was measured and found to be a dimer, as formulated. Formulation as a monomer results in a point significantly off the calibration curve.

Molecular weight determination by freezing point depression.[11] Sulfolane was used as the cryoscopy solvent due to its large molal freezing point depression constant (66.2 deg/mole).[12] The standard procedure was used employing a large test tube as the reaction vessel and a Bechman thermometer. The melting point of the solvent is 28.8°C, thus no artificial cooling is required.

The molecular weight of 13 was determined from two separate samples,

measured two times each. Based on molecular weight determinations of several known complexes of similar type, the error involved in this measurement is estimated to be 15%.

## Results and Discussion

The reaction of [Ir(CO)$_2$Br$_2$]$^-$ as its $\underline{n}$-Bu$_4$N$^+$ salt with the di(tertiary phosphine) ligands dppp and dppe serves as a convenient route to the formation of iridium(I) phosphine complexes. While both ligand systems react to form mononuclear species, only dppp is observed to form binuclear complexes as well.

### Binuclear dppp Complexes.

The room temperature reaction of [$\underline{n}$-Bu$_4$N][Ir(CO)$_2$Br$_2$] with dppp in acetone under N$_2$ leads to the evolution of CO and the essentially quantitative production of the pale yellow complex [Ir$_2$Br$_2$(CO)$_2$(dppp)$_2$], **8**.



|   |   |
|---|---|
| **8** | X = Br |
| **9** | X = I |
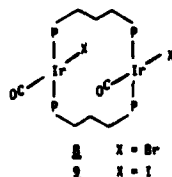
The dimeric structure of **8** is assigned based on elemental analyses, the $^{31}$P{$^1$H} nmr spectrum which shows only singlets indicative of $\underline{trans}$ P donors,[13] the IR spectrum, and by analogy with the chloro complex, **5**, first reported by Sanger.[3] An approximate molecular weight determination using Bio Bead filtration (see Experimental Section) indicates a molecular weight of $\underline{ca}$. 1400 for **8** consistent with its binuclear formulation. Conductivity measurements show **8** to be a nonelectrolyte in DMF solution. The CO ligands in **8** are shown in a cis orientation because two carbonyl stretches at 1944 and 1915 cm$^{-1}$ are observed in its IR spectrum. Both $\nu_{CO}$'s are indicative of terminal CO coordination to square planar Ir(I). Additional support for the structural assignment of **8** derives from its reaction with N$_2$ which gives an essentially quantitative

yield of a single, easily characterized binuclear product (vide infra). The infrared and $^{31}$P nmr spectral data for **8** and all following compounds are presented in Table I.

The iodo complex **9** is prepared by metathesis of iodide for chloride in complex **5**. This method was first used by Wang and Pignolet, who found that **9** prepared by this route has only a single carbonyl stretching frequency in the IR spectrum (at 1950 cm$^{-1}$).[6] Based on the single $\nu_{CO}$, **9** is assigned a structure with the CO ligands in the trans orientation as in the previously reported chloro complex **5**, but in contrast with the bromo analog **8**. Wang and Pignolet have also found **9** to have a $^{31}$P nmr spectrum containing only one sharp singlet at 14.0 ppm.

The oxidative addition of H$_2$ to **8** and **9** yields binuclear hydride complexes as shown in Eq.(4). Under 1 atm H$_2$ in CH$_2$Cl$_2$, **8** and **9** form the tetrahydride complexes **10** and **11**. The formation of **11** in THF at 25°C is essentially complete within 1 hour compared with 24 hours for the formation of **10** and only incomplete conversion of the chloro complex **5** to its tetrahydride **7** under the same conditions. This observation is consistent with the notion of increased

$$[IrX(CO)(dppp)]_2 + 2H_2 \longrightarrow \qquad\qquad (4)$$
$$X = Br,I$$



|   |   |
|---|---|
| **10** | X = Br |
| **11** | X = I |
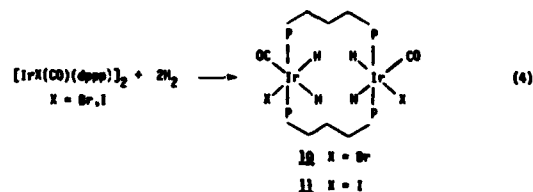
reactivity with halide ligand in the order Cl<Br<I. The same order of reactivity was found for the addition of H$_2$ to $\underline{trans}$-Ir(CO)X(PPh$_3$)$_2$, X=Cl,Br,I.[7]

The IR spectrum of 10 contains two $\nu_{CO}$'s (1945, 1980 cm$^{-1}$) while that of 11 contains only one (1980 cm$^{-1}$). The two $\nu_{CO}$'s of 10 change in relative intensity in solution indicating that they belong to different species. Since 10 is known to lose $H_2$ readily, we propose the $\nu_{CO}$ at 1945 cm$^{-1}$ to be due to iridium(I) carbonyl resulting from reductive elimination of $H_2$ at one of the iridium centers.

The $^1H$ nmr spectra of 10 and 11 provide key information about the structure of these complexes. The full $^1H$ nmr spectrum, from +10 to -20 ppm, of 10 is shown in Figure 1. There are three groups of resonances. The phenyl protons at ca. $\delta=7$ ppm are split into two groups - the ortho protons, and the meta + para phenyl protons. The methylene protons of the dppp ligand are split into two broad, symmetrical resonances. Homonuclear decoupling indicates that the broadness is due to phosphorus coupling. Last, the pair of triplets of doublets in the hydride region, expanded in the Fig. 1 inset, integrate as four protons compared to the twelve methylene protons, indicating a tetra-hydride.

The pair of triplets of doublets, separated by ca. 9 ppm, indicate that the hydride ligands are trans to very different ligands. The doublet splitting of 3 Hz is due to hydride-hydride coupling, as shown by homonuclear decoupling experiments. When each triplet of doublets is irradiated, the other one collapses to a simple triplet. This indicates that the hydride ligands are cis to each other. The triplet splitting is 13 Hz, and is due to the coupling of two equivalent P atoms to the hydride ligands. The P donors are therefore necessarily trans to each other and cis to the hydride ligands in 10 and 11.

The $^{31}P$ nmr of 10 consists of 2 sharp singlets in an approximately 4:1 ratio, and confirms the assignment of trans P ligands. The observation of two

singlets is consistent with the $^{31}P$ nmr spectra of 6 and 7 measured by Wang and Pignolet, who rationalized the minor resonance as due to the Ir(I) center of the Ir(I)-Ir(III) dimer formed by incomplete $H_2$ oxidative addition or reductive elimination of one mole of $H_2$ from the Ir(III)-Ir(III) tetrahydride, 7.[6] This explanation seems most satisfactory since both 7 and 10 lose $H_2$ easily, and 10 exhibits two $\nu_{CO}$'s in solution, one of which is attributable to iridium(I) carbonyl.

The $^1H$ and $^{31}P$ nmr spectral data for 10 and 11 are consistent with structure A about each Ir center in which the phosphine ligands are trans. The hydride ligand trans to CO gives rise to the resonance at -8.6 ppm, while the hydride trans to halide gives rise to the one at -18.7 ppm in the $^1H$ nmr spectrum. The assignment of the hydride resonances is by analogy to the



A
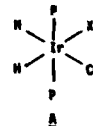
known mononuclear dihydride complexes, $IrH_2X(CO)(PR_3)_2$, X=Cl,Br,I, which possess geometry A, and whose $^1H$ nmr spectra have very similar hydride regions to 7, 10 and 11. For example, the hydride region in the $^1H$ nmr spectrum of $IrH_2Cl(CO)(P(CH_3)_2(Ph))_2$ contains two triplets of doublets at $\delta=-7.58$ and $\delta=-18.36$ ppm.[1a] For the complex $IrHCl_2(CO)(P(CH_3)_2(Ph))_2$, in which the hydride is known to be trans to the halide, the single triplet is found at -15.7 ppm.[1a] Thus the hydride at -18.36 ppm in $IrH_2Cl(CO)(P(CH_3)_2(Ph))_2$ is assigned as trans to chloride. Many similar examples have been tabulated and suggest the generality that hydride ligands trans to halides appear at considerably higher fields than those trans to carbonyl groups.[1a] The $^1H$ nmr spectral data for

IrH$_2$Br(CO)(PPh$_3$)$_2$, complexes 10 and 11, and related complexes which remain to be discussed are tabulated in Table II.
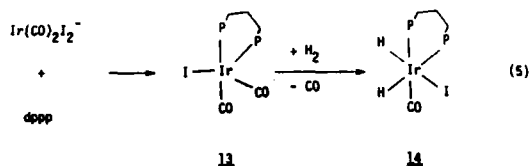
While optimizing the preparative procedure for 10, it was found that oxidative addition of only a single molecule of H$_2$ to 8 can be accomplished to form the Ir(I)-Ir(III) dihydride, 12, analogous to 6 reported by Pignolet and Wang.[6] In acetone, the reaction of 8 with H$_2$ yields a mixture of 10 and 12, as evidenced by the $^1$H nmr spectrum which contains three pairs of triplets of doublets. The pair at δ=-8.6 and -18.7 ppm is attributed to the tetrahydride, 10. The four new triplets of doublets are found at -8.4, -8.8, -18.2 and -18.8 ppm. When a sample of this mixture is sealed in an nmr tube under vacuum, and spectra recorded at hourly intervals, these new resonances are observed to gain intensity at the expense of the resonances assigned to the tetrahydride, 10. Homonuclear decoupling experiments relate the -8.4 ppm triplet to the -18.8 ppm triplet and the -8.8 ppm triplet to the -18.2 triplet, indicating the presence of two species in addition to 10. These two species correspond to two geometric isomers of the Ir(I)-Ir(III) dihydride complex 12. The addition of one equivalent of H$_2$ to a CH$_2$Cl$_2$ solution of 8 under H$_2$ also results in the formation of the pale yellow dihydride 12, and the $^1$H nmr spectrum of a sample of 12 prepared this way contains the four new triplets of doublets described above.

**Mononuclear Complexes.** A mononuclear Ir(I) dppp complex can also be formed from the reaction of Ir(CO)$_2$I$_2^-$ with dppp. The room temperature reaction of Ir(CO)$_2$I$_2^-$ with dppp leads to the evolution of CO and the isolation of an orange complex, 13. This complex exhibits two carbonyl stretching frequencies (2040, 1955 cm$^{-1}$) in both solution and solid state IR spectra, and shows only one singlet in the $^{31}$P nmr spectrum. A molecular weight determination

by freezing point depression yields a molecular weight of 715, indicating a mononuclear formulation for 13. Compound 13 is not air sensitive during short periods of exposure (<15 min). The complex reacts with H$_2$ in benzene over 24 h to form a new hydride complex 14, along with the evolution of CO.

This new hydride species 14 exhibits only one ν$_{CO}$ in the IR spectrum (see Table I) and has a very different $^1$H nmr spectrum than is observed for the dimeric hydrides 7, 10 and 11. The $^1$H nmr spectrum of 14 is shown in Fig. 2. The main features of the hydride pattern are two groups of resonances separated by ~6 ppm, one of which is a broad doublet of doublets and the other a more complicated multiplet. The spectrum is consistent with chemically different P nuclei, and the magnitude of the larger doublet-of-doublets splitting (J$_{P-H}$ = 120 Hz) suggests that one of the hydrides is trans to a phosphine donor. The second hydride is located trans to iodide based on its chemical shift. In addition, the $^{31}$P nmr spectrum of 14 consists of two doublets with 30.5 Hz coupling, indicative of two chemically inequivalent cis P ligands.

The spectroscopic data provide the basis for a consistent interpretation of the reactions involving Ir(CO)$_2$I$_2^-$ + dppp and H$_2$ as shown in Eq.(5). The initial product having ν$_{CO}$ of 2040 and 1955 cm$^{-1}$ is mononuclear, unlike the other dppp complexes formed in analogous reactions. The two carbonyl stretches indicate a cis disposition of CO ligands in the complex. This complex, IrI(CO)$_2$(dppp), is thus assigned structure 13 with a chelating di(tertiary phosphine) ligand. The singlet in the $^{31}$P nmr spectrum of 13 is due to the stereochemical nonrigidity of this five coordinate d$^8$ species. The reaction of 13 with H$_2$ leads to loss of CO, which is detected in the gas phase above the solution, and helps confirm the formulation of 13 as a mononuclear dicarbonyl complex. The reaction with H$_2$ leads to the formation of 14

$$Ir(CO)_2I_2^- \; + \; dppp \;\longrightarrow\; [\text{structure } 13] \;\xrightarrow[- CO]{+ H_2}\; [\text{structure } 14] \qquad (5)$$

$$\underline{13} \qquad\qquad \underline{14}$$

which possesses structure B, and gives rise to one $\nu_{CO}$ and one $\nu_{Ir-H}$ in the IR. An alternative binuclear formulation of $\underline{14}$ with bridging dppp ligands in cis positions of the coordination sphere is ruled out based on highly unfavorable steric interactions between neighboring diphenylphosphino groups, the mononuclear nature of $\underline{13}$, and parallel reaction chemistry observed using dppe which is discussed below.

*Cleavage of Binuclear dppp Hydrides.* The mononuclear dppp dihydride $\underline{14}$, and its bromoanalog, $IrH_2Br(CO)(dppp)$, $\underline{15}$, can also be formed by cleaving the binuclear tetrahydrides $\underline{10}$ and $\underline{11}$. When $CH_2Cl_2$ or THF solutions of $\underline{10}$ and $\underline{11}$ are heated in the presence of $NEt_3$ a striking change occurs in the hydride region of the $^1H$ nmr spectra after 2-5 hours for $\underline{10}$ and 12-24 hours for $\underline{11}$. Specifically, the resonances characteristic of the trans P donors of $\underline{10}$ and $\underline{11}$ are replaced by those consistent with the cis P donors shown for $\underline{14}$. The change from trans to cis P donors occurs with a cleavage of the binuclear hydride system to the mononuclear structure $\underline{13}$ as shown in Eq.(6). The cleavage of $\underline{10}$ can also be effected by prolonged heating of $\underline{10}$ under Ar or $CO_2$ (24 Hours).

$$[\text{structure } 10] \;\longrightarrow\; [\text{structure } 15] \qquad (6)$$

$$\underline{10} \qquad\qquad \underline{15}$$
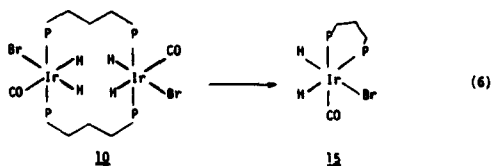
When a similar experiment was carried out with $\underline{11}$, the complex decomposed during the 24 hour experiment.

The lack of integrity of $\underline{10}$ as a binuclear species was surprising since Pignolet and Wang have employed $\underline{5}$ as a decarbonylation catalyst at 150°C, and have not observed dimer cleavage.[6] Moreover, reactions of similar complexes having dppm bridges under a variety of conditions have revealed no tendency of these dimers to break apart into monomeric species.[5] Our observation of dimer cleavage provides an important caveat to studies based on using di- and poly(tertiary phosphine) ligands to hold two or more metal atoms together in systems having structural integrity.

*dppe Complexes.* In order to provide additional support for the structural assignments of $\underline{13}$-$\underline{15}$ as mononuclear species, the analogous complexes with dppe in place of dppp were synthesized and characterized. The ligand dppe shows a much greater tendency towards chelation than does dppp, and only rarely forms a bridge between two metals.[15] The new mononuclear mono(dppe) complexes $Ir(CO)X(dppe)$, $\underline{16}$ (X=Br) and $\underline{17}$ (X=I), are prepared by reacting $[\underline{n}-Bu_4N][Ir(CO)_2X_2]$ with dppe in THF or benzene according to Eq.(7). Formation of $Ir(CO)(dppe)_2^+$, $\underline{3}$, cannot be avoided in this reaction, but the two different products can be easily separated because of their greatly different solubilities.

$$(n-Bu_4)[IrX_2(CO)_2]^- \; + \; dppe \;\longrightarrow\; [\text{structure}] \qquad (7)$$

$$\underline{16} \quad X = Br$$
$$\underline{17} \quad X = I$$
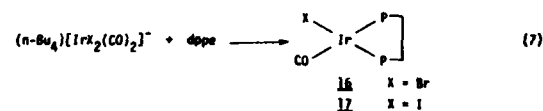
Complexes $\underline{16}$ and $\underline{17}$ have very similar spectroscopic properties (see Table I). The single $\nu_{CO}$ of 1980 cm$^{-1}$ for $\underline{16}$ and 1980 cm$^{-1}$ for $\underline{17}$ and the two doublets

in the $^{31}$P nmr spectrum of each complex provide good evidence that 16 and 17 are mononuclear mono(dppe) species. It is surprising that complexes 16 and 17 have not been reported previously since they are cis phosphine analogs of the well studied systems trans-IrX(CO)L$_2$ where L is a tertiary phosphine.

Solutions of the orange, square planar Ir(I) complexes 16 and 17 in THF or CH$_2$Cl$_2$ react rapidly with H$_2$ to form the mononuclear dihydride species 18 and 19, respectively. These complexes are readily isolated as colorless crystals

18    X = Br
19    X = I
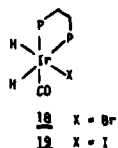
by the addition of EtOH and removal of solvent under a stream of H$_2$. The Ir(III) dihydride complexes 18 and 19 as isolated are considerably less soluble than their Ir(I) precursors. However, they do lose H$_2$ on standing in air. Complexes 18 and 19 are spectroscopically similar to complexes 14 and 15 (see Tables I and II). The $^1$H nmr spectrum of 18 is shown in Fig. 3 and an expanded view of the hydride region is shown in the inset. The "downfield" hydride resonance is a doublet of doublets of doublets ($J_{H-P_{trans}}$ = 130 Hz; $J_{H-P_{cis}}$ = 17 Hz; $J_{H-H}$ = 4.5 Hz), and is separated from the "upfield" hydride multiplet by 9 ppm. Irradiation of the upfield multiplet results in loss of the smallest doublet splitting in the downfield hydride resonances, leaving a doublet of doublets pattern. The observation of hydride-hydride coupling for 18 and 19 represents the only difference in their $^1$H nmr spectra from those observed for the analogous dppp complexes, 14 and 15.

An intriguing aspect of the H$_2$ oxidative addition to 16 and 17 is that

it is not only extremely facile, but also stereospecific. The initial product formed is an isomer of 18 or 19, which contains one hydride trans to CO and the other trans to P. This material then isomerizes to the product as drawn above, and shown in Fig. 3. A detailed examination of this observation will be reported in a separate paper.[16]

Complexes 16 and 17 also react with CO to form dicarbonyl species 20 and 21 analogous to 13. These complexes exhibit two $\nu_{CO}$'s at 1940 and 2040 cm$^{-1}$ for 20 and 1950 and 2040 cm$^{-1}$ for 21. The $^{31}$P nmr spectrum of each complex exhibits only one sharp singlet at room temperature, in accord with that observed for the dppp complex 13, suggesting that these five-coordinate $d^8$ species are stereochemically nonrigid at room temperature.

Both H$_2$ oxidative addition and CO addition to 16 and 17 are reversible. Refluxing THF or benzene solutions of these adducts under N$_2$ leads to loss of the addend molecule and regeneration of 16 or 17. Because of the extreme facility with which 20 and 21 lose CO, attempts to isolate analytically pure samples of these compounds were unsuccessful. However, the dicarbonyl compounds were completely characterized by solution spectroscopic methods. It is interesting to note that Vaska's complex, trans-IrCl(CO)(PPh$_3$)$_2$, also reversibly binds CO to give a dicarbonyl complex,[17] but the forward reaction is not as rapid as that observed for 16 or 17.

In summary, the synthesis and characterization of iridium hydrides having the di(tertiary phosphine) ligands dppp and dppe as bridges and chelates have been examined. Binuclear dppp bridged complexes of formula [IrH$_2$X(CO)(dppp)]$_2$ where X = Br, I possess the phosphine donors in trans disposition as shown by $^1$H nmr spectroscopy. Upon heating, these dimers cleave into monomeric species of the same stoichiometry in which dppp acts as a chelate. The dppe complexes are all mononuclear, and contain a dppe chelated ring. The hitherto unreported

complexes [rX(CO)(dppe) where X = Br, I have been described as has their reaction chemistry to form reversible adducts with $H_2$ and CO.

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13. The $^{31}P$ nmr spectrum of a freshly prepared sample of 8 consists of three sharp singlets. The two major singlets are at $\delta = 19.03$ and $-5.36$ ppm downfield of $H_3PO_4$ and are of equal intensity. The third singlet is small and is found at 18.3 ppm. No additional resonances were observed in a 16,000 Hz spectrum centered at 0 ppm, ruling out the possibility that the two peaks at 19.03 and -5.36 ppm are a doublet with the characteristically large trans phosphorus coupling. In addition, the singlets are 3000 Hz apart, while typical trans P coupling is 300-600 Hz. Upon standing at room temperature, the singlets at 19.03 and -5.36 ppm lose intensity equally to the singlet at 18.3 ppm. Thus it seems plausible that the pair of singlets at +19.03 and -5.36 ppm are due to cis-8 and the singlet at 18.6 ppm is due to the trans complex. However, we have no ready explanation for this spectrum. Considerable disagreement exists in the literature concerning the $^{31}P$ nmr and IR spectra of similar complexes. Two different investigators report two different $^{31}P$ nmr spectra

for 5.[3,6] In addition, [RhCl(CO)(dppm)]$_2$ has been reported as both cis and trans, but a consistent set of IR and $^{31}$P spectral data for the two isomers was never obtained.[14]

The evidence for the formulation of 8 as drawn is primarily in its reaction with H$_2$ (vide infra), which gives an essentially quantitative yield of a single, easily characterized dimeric product.

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Table 1

Infrared and $^{31}$P NMR Spectral Data for Iridium dppp and dppe Complexes

| Compound | IR(cm$^{-1}$)[a] | | $^{31}$P nmr |
|---|---|---|---|
| | $\nu_{CO}$ | $\nu_{Ir-H}$ | |
| [Ir$_2$Br$_2$(CO)$_2$(dppp)$_2$]<br>8 | 1915,1944 | | 19.03(s),18.6(s),-5.3(s)[d] |
| [Ir$_2$I$_2$(CO)$_2$(dppp)$_2$]<br>9 | 1950 | | 14.0(s)[e] |
| [Ir$_2$H$_4$Br$_2$(CO)$_2$(dppp)$_2$]<br>10 | 1945,1980 | 2100,2190 | 0.04(s),0.47(s)[d] |
| [Ir$_2$D$_4$Br$_2$(CO)$_2$(dppp)$_2$]<br>10, D$_4$ | 2016 | b | - |
| [Ir$_2$H$_4$I$_2$(CO)$_2$(dppp)$_2$]<br>11 | 1980 | 2090,2160 | |
| [Ir$_2$H$_2$Br$_2$(CO)$_2$(dppp)$_2$]<br>12 | 1945,1980 | 2100,2190 | |
| IrI(CO)$_2$(dppp)<br>13 | 1955,2040 | | -28.49(s)[d] |
| IrH$_2$I(CO)(dppp)<br>14 | 2042 | 2105 | 21.9(d),29.9(d)[d]<br>J$_{p-p}$=30.52 Hz |
| IrH$_2$Br(CO)(dppp)<br>15 | 2043 | 2220 | |
| IrBr(CO)(dppe)<br>16 | 1980 | | 43.7(d),47.9(d)[c]<br>J$_{p-p}$=14 Hz |
| IrI(CO)(dppe)<br>17 | 1980 | | 64.3(d),62.21d[c]<br>J$_{p-p}$=9.5 Hz |
| IrH$_2$Br(CO)(dppe)<br>18 | 2030 | 2195 | 33.8(d),26.6(d)[c] |
| IrH$_2$I(CO)(dppe)<br>19 | 2040 | 2160 | 28.06(d),20.62(d)[d]<br>J$_{p-p}$=7 Hz |
| IrBr(CO)$_2$(dppe)<br>20 | 1940,2040 | | 53.51(s)[c] |
| IrI(CO)$_2$(dppe)<br>21 | 1950,2040 | | 32.0(s)[c] |

Table I (Continued)

[a]IR Spectra were recorded on a Perkin-Elmer 467 Grating Infrared Spectrophotometer. All spectra were taken of KBr pellets except for 13, 20 and 21 which were in benzene solution.

[b]$\nu_{IR-D}$ not observed.

[c]Measured in 5 mm tubes on Bruker WM-400 at 162 MHz. Positive chemical shifts are downfield from $H_3PO_4$ (external).

[d]Measured in 10 mm tubes on JEOL FFT-100 spectrometer at 41.25 MHz.

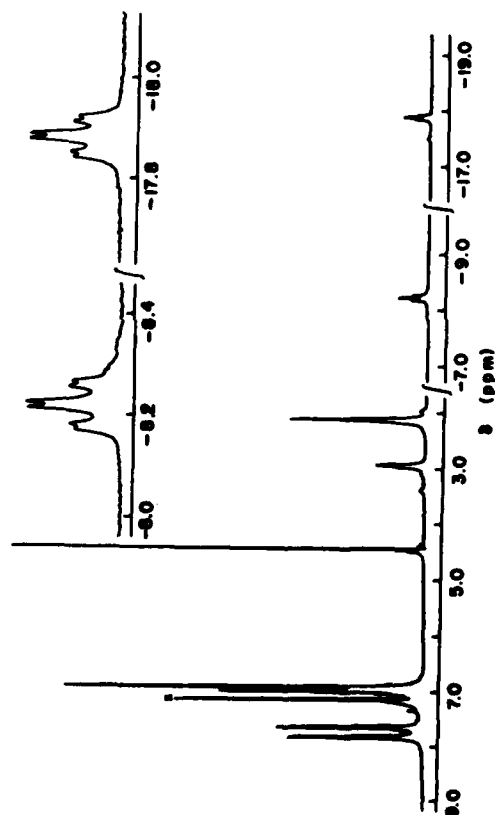[e]Measured by Wang and Pignolet (see Ref. 6).

Table II

^{1}H NMR Spectral Data for Iridium dppp and dppe Hydride Complexes
(Hydride Region Only)

| Compound | ^{1}H NMR |
|---|---|
| $IrH_2Br(CO)(PPh_3)_2$ | -7.35 (t of d), $J_{PH-cis}$ = 17.5 Hz, $J_{HH}$ = 4.5 Hz; -16.53 (t of d), $J_{PH-cis}$ = 13.7 Hz, $J_{HH}$ = 4.5 Hz (CDCl$_3$) |
| $[Ir_2H_4Br_2(CO)_2(dppp)_2]$ **10** | -8.6 (t of d), -18.7 (t of d) (CDCl$_3$) $J_{PH-cis}$ = 13 Hz, $J_{HH}$ = 3 Hz |
| $[Ir_2H_4I_2(CO)_2(dppp)_2]$ **11** | -9.74 (t of d), -16.84 (t of d) (CDCl$_3$) $J_{PH-cis}$ = 13 Hz, $J_{HH}$ = 3 Hz |
| $[Ir_2H_2Br_2(CO)_2(dppp)_2]$ **12** | -8.4, -8.8, -18.2, -18.8 (all t of d) (CDCl$_3$) $J_{PH-cis}$ = 13 Hz, $J_{HH}$ = 3 Hz |
| $IrH_2I(CO)(dppp)$ **14** | -9.27 (d of d), $J_{PH-trans}$ = 120 Hz, $J_{PH-cis}$ = 16 Hz), -15.35 (m) (C$_6$D$_6$) |
| $IrH_2Br(CO)(dppp)$ **15** | -9.27 (d of d), $J_{PH-trans}$ = 120 Hz, $J_{PH-cis}$ = 16 Hz), -17.99 (m) (C$_6$D$_6$) |
| $IrH_2Br(CO)(dppe)$ **18** | -9.05 (d of d of d, $J_{PH-cis}$ = 17 Hz, $J_{PH-trans}$ = 130 Hz, $J_{HH}$ = 4.5 Hz), -18.26 (m) (CDCl$_3$) |
| $IrH_2I(CO)(dppe)$ **19** | -9.92 (d of d of d, $J_{PH-cis}$ = 17 Hz, $J_{PH-trans}$ = 128 Hz, $J_{HH}$ = 4.5 Hz), -16.27 (m) (acetone$_{d-6}$) |

All proton nmr spectra recorded on a Bruker WM-400 at 400.134 MHz. Positive chemical shifts are downfield from TMS.

### Figure Captions

Figure 1. $^1H$ nmr spectrum of $[Ir_2H_4Br_2(CO)_2(dppe)_2]$, 10, in $C_6D_6$. The resonance labelled X is $C_6D_5H$. The resonance at 4.46 ppm is dissolved $H_2$. The inset is an expanded view of the hydride region.

Figure 2. $^1H$ nmr spectrum of $[IrH_2I(CO)_2(dppe)]$, 14, in $C_6D_6$. The resonance labelled X is an impurity in the solvents. The resonance at 4.46 ppm is dissolved $H_2$. The inset is an expanded view of the hydride region.

Figure 3. $^1H$ nmr spectrum of $[IrH_2Br(CO)(dppe)]$, 18, in $C_6D_6$. The resonance at 4.46 ppm is dissolved $H_2$. The inset is an expanded view of the hydride region.
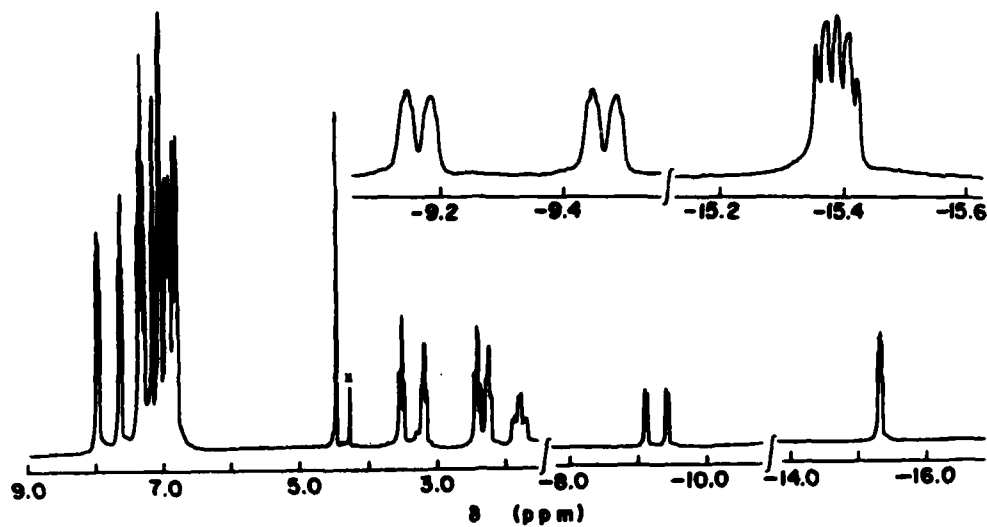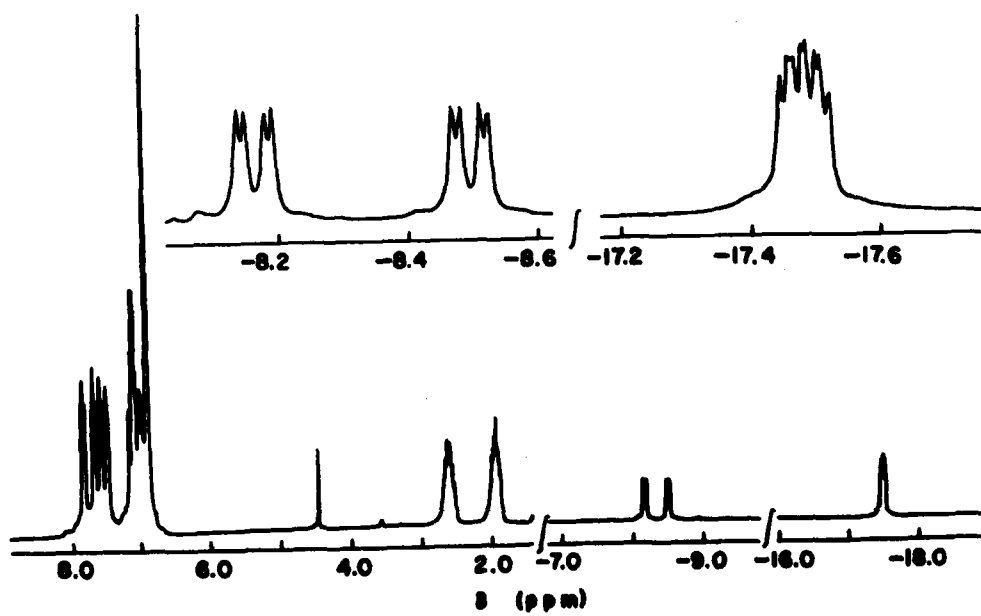


Figure 1

Figure 3

# END

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